INVESTIGATION OF PULSED NON-MELT LASER ANNEALING (NLA) OF CIGS-BASED SOLAR CELLS

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ABSTRACT

Pulsed Non-melt Laser Annealing (NLA) has been used to modify the near surface defect density and related junction properties in CIGS solar cells. CIGS films deposited on Mo/glass substrates were annealed by the NLA technique at selected laser energy densities and pulse number, and characterized by the Dual Beam Optical Modulation (DBOM), XRD, SEM, and Hall measurements. In addition, selected annealed CIGS/CdS films processed by NLA were fabricated into cells, and characterized by the photo I-V and Q-E measurements. The results suggest that low power NLA treatment could enhance the effective carrier lifetime, mobility, film grain size, and sheet resistance and lower the near-surface defect density in the films, thus improve the performance of CIGS cells.

1. Introduction

Non-melt Laser Annealing (NLA) is widely used to activate boron ion implants in Si wafers and to remove undesirable boron clustering, defect evolution, and damage to the lattice created by implant. The possibility of using this approach to modify defects in CIGS based films was motivated by the positive results reported for NLA processing of Si wafers. The basic idea is to promote atom mobility by local heating on the nanometer length scale and thus confine the impact of processing to the near-junction region of the device. The results from characterizing CIGS films and cells suggest that interfacial recombination near the CIGS/CdS metallurgical junction is a major limitation to optimal device performance. NLA treatment promises to permit annealing of defects in the near surface region, while preserving the beneficial composition gradients in the CIGS films.

2. Preliminary characterization results of Non-Melt Laser Annealed CIGS films

Laser annealing of CIGS and CIGS/CdS samples was performed using a 248 nm line Kr Excimer laser, operated with a pulse width of 25 ns, and energy density in the range of 20 to 60 mJ/cm^2. The non-destructive Dual Beam Optical Modulation (DBOM) technique developed in Dr. Li's lab was used to measure the effective carrier lifetimes in the CIGS absorber [1, 2], and to evaluate the effect of NLA on the performance of CIGS cells. Within the sensitivity of the DBOM measurement, the effective carrier lifetimes were found to increase for CIGS films annealed with 5 pulses laser beam each having an energy density in the range of 30 to 60 mJ/cm^2. The results shown in Table 1 indicate that low power NLA treatments increase the effective lifetimes of the annealed samples. The relationship between the energy density of the laser beam and the increase of effective carrier lifetime is still unclear. XRD analysis of CIGS and CIGS/CdS samples before and after laser annealing (see Figure 1) revealed sharper peaks attributable to the CIGS phases, consistent with increased crystallinity. As illustrated by SEM micrographs displayed in Figure 2, the surface morphology and apparent grain size changed upon laser annealing. This result suggests that the energy density was sufficient to cause atomic rearrangement in the near surface region, and thus the potential for modifying the atomic defects in the region.

Sample #	Carrier lifetime (before NLA)	Carrier lifetime (after NLA)	NLA condition
CIGS#1	1.77 ns	4.87 ns	30m J/cm^2, 5 pulses
CIGS#2	2.82 ns	3.39 ns	40m J/cm^2, 5 pulses
CIGS#3	4.1 ns	5.43 ns	50m J/cm^2, 5 pulses
CIGS#4	4.5 ns	6.31 ns	60m J/cm^2, 5 pulses

Table 1. Effective lifetimes of NLA CIGS samples.

3. The Hall- effect, I-V and Q-E measurements of NLA CIGS films and cells

Based on the encouraging DBOM results from the initial NLA treatment of CIGS samples, a second set of experiments was performed in which the energy density and pulse number of the incident laser radiation were varied. Hall effect, I-V and Q-E measurements were made on the CIGS samples prior and after annealing to determine the effect of NLA treatment on the carrier concentration, resistivity, and photo-response of the cells.

3.1 The Hall- effect measurements:

Four CIGS films deposited on the glass substrate were treated with pulsed NLA at room temperature. The annealing conditions and the results of Hall effect measurements are summarized in Table 2. These results show a significant increase in the value of Hall mobility and decrease in film resistivity after NLA treatment. The carrier mobilities of the NLA treated samples were found 3 to 4 times greater than the values before annealing. Although the hole density was found to decrease slightly with annealing, the film resistivity was decreased by 72% and 64% for the samples treated at an energy density of 20 mJ/cm^2 (samples 1H and 2H, respectively). At a higher energy density of 40 mJ/cm^2 the film resistivity was changed by almost half the unannealed value (samples 3H and 4H). Thus, both the energy density and the number of pulse cycle of the laser beam could play an important role in determining the resistivity of CIGS absorber layers.

3.2 The Photo- I-V measurements:

Four CIGS/CdS samples were annealed by a 50 mJ/cm^2 laser beam with different pulse number. Two samples were followed by a 100 Å extra CdS buffer layer re-growth after NLA treatment on the CIGS samples initially coated with a 400 Å CBD CdS buffer layer, and one control sample without any treatment. These samples were then fabricated into cells for testing. The DBOM and photo- I-V results are summarized in Table 3, which show an increase in the effective carrier lifetimes on the NLA treated samples. No explicit improvements, however, were found in the photo- I-V results of the annealed cells. The data also show slight decreasing in the fill factor and conversion efficiency of cells annealed with 20 pulses NLA compared with the 10-pulse-annealed cells. Some high energy density (i.e., 80 mJ/cm^2) NLA treatments were also used on other CIGS samples, and the results show a drastic reduction in the cell efficiency. These results suggest that an optimal NLA energy density should be less than 50 mJ/cm^2, and no significant influence on the cell performance due to the additional CdS buffer layer re-growth was found in this study.

3.3 The Q-E measurements:

Two CIGS films with a 500 Å CdS buffer layer were annealed at an energy density of 50 mJ/cm^2, and then fabricated into cells. To study the effect of pulsed NLA treatment, the spectral response and quantum efficiency (Q-E) were measured on these cells. The results shown in Figures 3 and 4 indicate that for incident light with wavelengths greater than 630 nm, the Q-E and spectral response of the NLA cells are higher than those of the control cell, indicating that the NLA treatment increases the effective carrier lifetime and diffusion length in the absorber layer and hence increases the short-circuit current density in comparison to the control cell without NLA treatment. In the short wavelength regime ($\lambda < 0.65$ μm), however, the Q-E and spectral response decrease after NLA treatment, which suggest damages near the interface region of CIGS/CdS films by the laser beam. As a result, the surface recombination velocity is increased and the Q-E and spectral response are lower in the shorter wavelength region. It is also noted that the values of Q-E and spectral response for sample annealed with 20 cycles laser pulse were found to be lower then the sample with 10 cycles of annealing pulse with same energy density.

4. Conclusions

The effect of pulsed NLA treatment on the CIGS-based solar cells was investigated under selected annealing conditions. Several characterization techniques (DBOM, XRD, SEM, Hall-effect, I-V and Q-E measurements) support the conclusion that pulsed NLA treatment at certain conditions has a positive effect on the effective carrier lifetime, mobility, surface morphology, spectral response and hence on the device performance. The energy density of the laser beam and the number of pulse cycle play a central role in modifying the optical and electrical properties of the CIGS absorbers. Future efforts will be focusing on optimization of the pulsed NLA energy density and annealing cycle for improving the cell performance.

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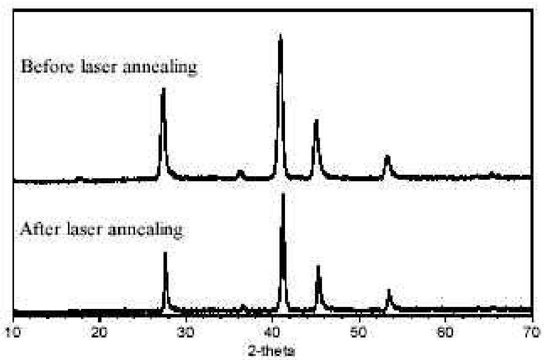
sample #	Before NLA			After NLA				
	Hole density (cm^{-3})	Hall mobility (cm^2/V-s)	Resistivity (Ω-cm)	Energy Density (mJ/cm^2)	Pulse #	Hole density (cm^{-3})	Hall mobility (cm^2/V-s)	Resistivity (Ω-cm)
#1H	$5.3*10^{15}$	8.89	133	20	10	$4.45*10^{15}$	37.6	37.3
#2H	$2.9*10^{16}$	0.93	235	20	20	$2.43*10^{16}$	2.977	86.4
#3H	$4.3*10^{16}$	1.54	94	40	10	$1.8*10^{16}$	6.1	2.67
#4H	$7.1*10^{16}$	0.60	148	40	20	$3.3*10^{16}$	2.8	4.64

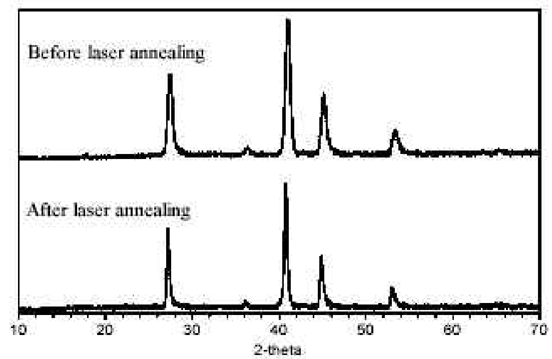
Table 2. Results of Hall effect measurements on laser annealed (NLA) CIGS samples.

Sample #	Lifetime(ns)	Vo (V)	Jsc(mA/cm^2)	F.F.(%)	Eff.%	NLA condition
CIGS/CdS #0	3.76	0.42	27.2	53.11	6.14	Control sample
CIGS/CdS #1	4.77	0.45	24.83	54.43	6.17	50mJ/cm^2, 10 pulses
CIGS/CdS #2	4.11	0.44	26.98	51.37	6.15	50mJ/cm^2, 20 pulses
CIGS/CdS #3	5.2	0.45	26.19	54.06	6.27	50mJ/cm^2, 10 pulses w/CdS re-growth
CIGS/CdS #4	3.86	0.39	26.43	44.25	4.57	50mJ/cm^2, 20 pulses w/CdS re-growth

Table 3. Effective lifetimes and I-V results of NLA CIGS/CdS samples and devices.

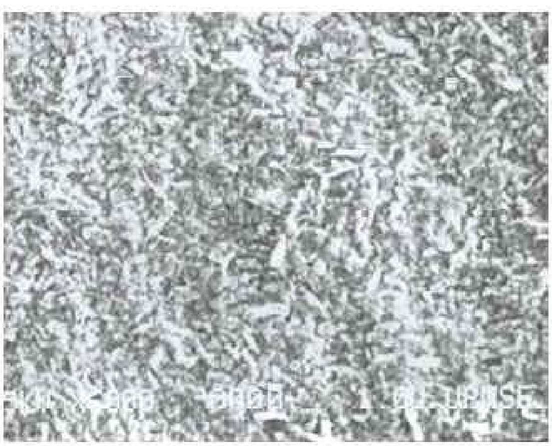


(a)

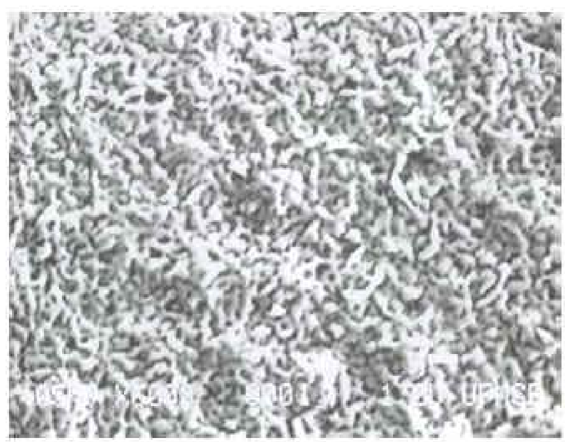


(b)

Figure 1. XRD spectra of (a) CIGS sample and (b) CIGS sample coated with a 500Å CdS layer before and after laser annealing.



(a)



(b)

Figure 2. Characteristic surface morphology of CIGS films (a) without and (b) with laser annealing at an energy density of 55 mJ/cm^2(SEM images with magnification of 6000x).

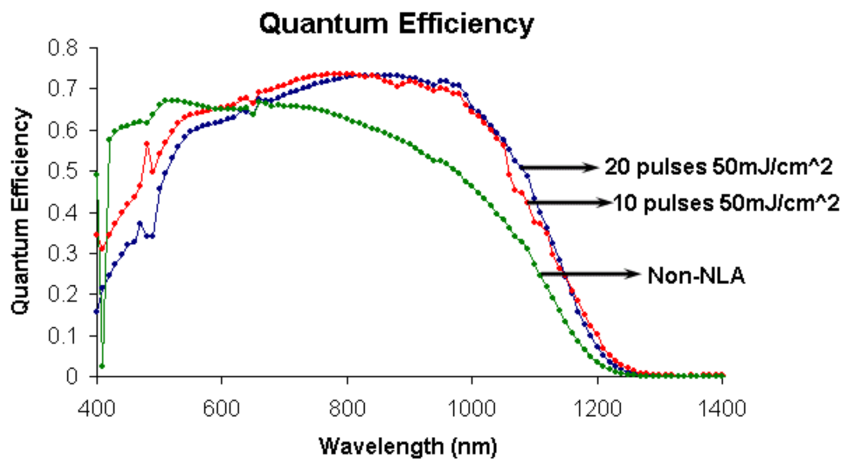


Figure 3. Quantum efficiency of CIGS cells with and without NLA treatment.

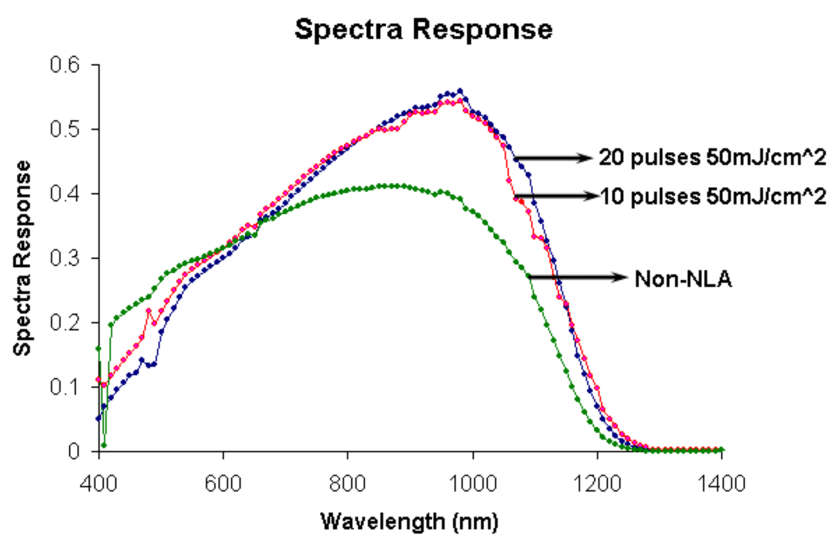


Figure 4. Spectral response of CIGS cells with and without NLA treatment.